

# Direct identification of photofragment isomers: the photodissociation of propyne at 193nm.

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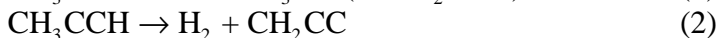
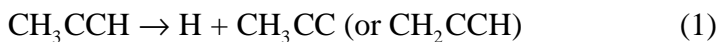
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The  $C_3H_3$  radical, an important molecule in hydrocarbon combustion,<sup>1-5</sup> has been proposed as the critical intermediate leading to the first aromatic ring in soot formation during combustion.<sup>3,6</sup> It is also an important radical in interstellar chemistry.<sup>7-8</sup> Astronomers have found  $C_3$  formation in comets, as well as cyclopropenylidene, which is currently thought to be the most abundant hydrocarbon in interstellar space.<sup>9-12</sup> However, the particular structure of the  $C_3H_3$  radical produced from dissociation of precursors having the form  $C_mH_nX$  ( $X=Cl, Br, CN\dots, H$ ) is still an open question. In 1966, Ramsay and Thistlethwaite<sup>13</sup> found that the flash photolysis of allene, propyne and  $XCH_2CCH$  ( $X=Cl, Br, CH_3\dots$ ) gave the same spectrum as the  $CH_2CCH$  radical molecule. These results suggested that either the other  $C_3H_3$  isomers have a lifetime shorter than 25 ns or all the precursors produced the  $C_3H_3$  as the lowest energy form, the propargyl radical ( $H_2CCCH$ ). These suggestions appeared reasonable, since the acetylenic C-H bond energy is 130 kcal/mol, much higher than the C(1)-H bond energy of 89 kcal/mol.<sup>14</sup> However, in 1991, two studies were performed which indicated that photodissociation of propyne ( $H_3CCH$ ) breaks the much stronger acetylenic C-H bond. The evidence was indirect, however, and the product isomer was not directly identified, so that rearrangement of the initially formed radical to the lowest energy form could not be ruled out.<sup>14,15</sup> Also in 1991, Y. T. Lee's group studied allene photolysis at 193 nm. The results suggested that the product  $C_3H_3$  in that case is the internally excited propargyl radical.<sup>16</sup>

We have used the technique of photofragment translational spectroscopy on Endstation 1 of the Chemical Dynamics Beamline 9.02, to complement laboratory studies of the dissociation dynamics of propyne following absorption at 193 nm. The technique uses a supersonic molecular beam of reactant seeded in neon, which is crossed at 90 degrees with the output of an excimer laser operating on the ArF transition (193.3 nm). The photoproducts that recoil out of the molecular beam are ionized by tunable undulator radiation, then mass selected by means of a quadrupole mass filter. Finally, the angle-resolved time-of-flight mass spectra are recorded. The use of tunable VUV undulator radiation is critical to an unambiguous identification of the chemical structure of the products as shown below.

We have directly observed follow dissociation channels:



The secondary photodissociation channels have also been observed:



We did not get distinguishable signal for the following channel, which was found by others<sup>12,14</sup>:



This indicated that channel (7) in our experiments should be less than 0.06% of all channels, which is determined by limitations of the detector used in these experiments.

Time-of-flight spectra were obtained on a laboratory instrument using photofragment translational spectroscopy with electron bombardment ionization. Product translational energy distributions for mass 39 ( $\text{C}_3\text{H}_3$ ) and 38 ( $\text{C}_3\text{H}_2$ ) were obtained from these distributions. However, identification of the product  $\text{C}_3\text{H}_3$  structure is very important to understanding basic isomerization processes of hydrocarbon reactions. The use of soft ionization by tunable undulator radiation on the Chemical Dynamics Beamline at the Advanced Light Source (ALS) allows for direct determination of the product structure. Figure 1a shows the photoionization efficiency (PIE) spectra for the  $\text{C}_3\text{H}_3$  product from propyne photolysis, and figure 1b shows the  $\text{C}_3\text{H}_3$  product from allene photolysis, both at 193nm. The ionization of  $\text{C}_3\text{H}_3$  from the photolysis of the two different precursor molecules shows very different probe photon energy dependence. The ionization onset from the PIE spectrum of  $\text{C}_3\text{H}_3$  from propyne photolysis is higher than 10 eV; in fact very close to the calculated  $\text{CH}_3\text{CC}$  IP of 11 eV. Meanwhile, the PIE spectrum of

$\text{C}_3\text{H}_3$  from allene photolysis indicated an onset consistent with formation of propargyl radical (8.67 eV). These experimental results strongly suggest that the photodissociation of propyne at 193 nm breaks the acetylenic C-H bond, clearly forming the propynyl radical. The available energy of this channel should be less than 20 kcal/mol. The very weak lower photon energy curve in Fig 1a may come from allene impurity in the propyne sample (about 2.4% allene impurity in propyne) or possibly from a very small amount of propargyl radical produced directly from photolysis. This

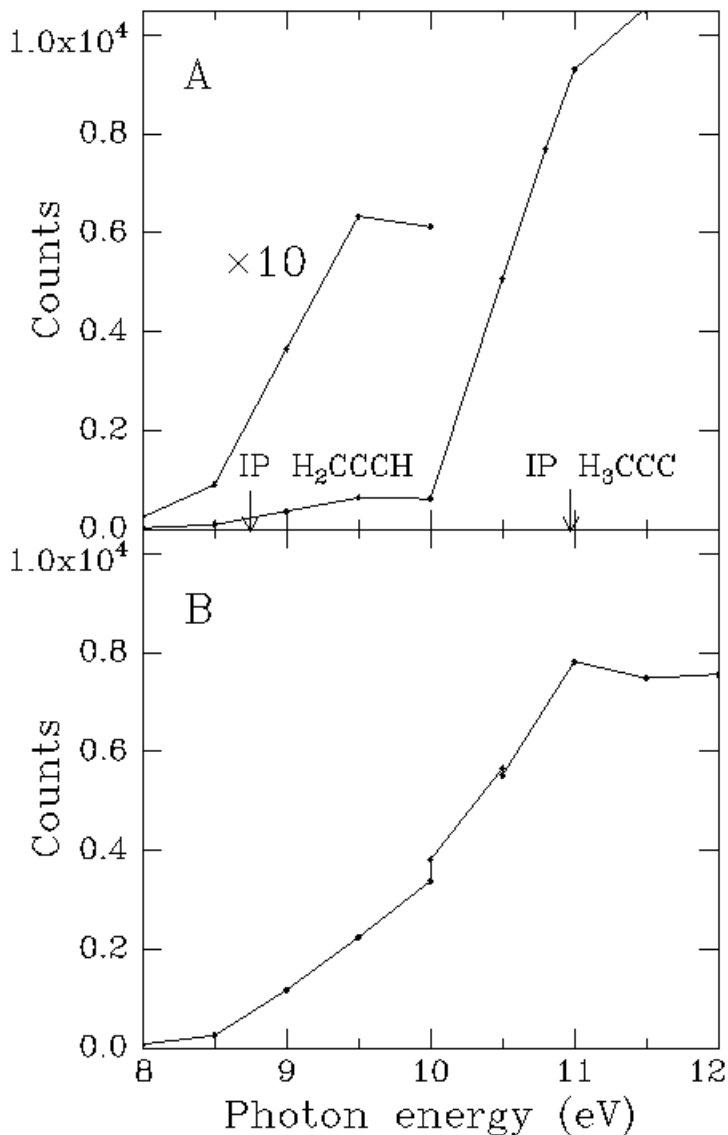


Figure 1. Photoionization efficiency spectra for mass 39 product from photolysis of propyne (A) and allene (B) at 193nm.

explains why Ramsay and Thistlethwaite did not observe an isotopic shift in the flash photolysis of  $\text{CH}_3\text{CCH}$  and  $\text{CH}_3\text{CCD}$ , since both precursors will give the same propynyl radical product.

These results demonstrate the unique capabilities of the combination of tunable VUV probe with photofragment translational spectroscopy to reveal otherwise inaccessible features of hydrocarbon dissociation dynamics. Further, the results show clear bond selective chemistry operating in the photolysis of propyne, where the much stronger acetylenic C-H bond is broken. This is likely owing to the localization of the electronic transition on the pi-bond system of the molecule, which then couples directly to the adjacent C-H bonds rather than to the remote C-H bonds in the methyl group.

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